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#### Organosiloxane-oxyalkylene copolymers

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#### **Abstract**

Organosiloxane-oxyalkylene copolymers in which at least one silicon atom of an organosiloxane unit has

attached thereto a group in which X is a divalent hydrocarbon group, R is an alkylene group, n is an integer of at least 2, Z is an organic substituent containing an epoxy group, R' is lower alkyl, vinyl or phenyl, R' is alkyl or alkoxyalkyl and a is 0 or 1, at least 40 percent of the total substituents in the copolymer being methyl. The copolymers are film forming and may be applied to continuous or porous substrates from aqueous or non-aqueous solutions.

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- (54) Organosiloxane-oxyalkylene copolymers
- (57) Organosiloxane-oxyalkylene copolymers in which at least one silicon atom of an organosiloxane unit has attached thereto a group

Z | -X(OR),OSiR',(OR'')<sub>2-e</sub>

in which X is a divalent hydrocarbon group. R is an alkylene group, n is an integer of at least 2, Z is an organic substituent containing an epoxy group, R' is lower alkyl, vinyl or phenyl, R' is alkyl or alkoxyalkyl and a is 0 or 1, at least 40 percent of the total substituents in the copolymer being methyl.

The copolymers are film forming and may be applied to continuous or porous substrates from aqueous or non-aqueous solutions.

#### **SPECIFICATION**

#### Organosiloxane-oxyalkylene copolymers

5 This invention relates to copolymers comprising organosiloxane units and oxyalkylene units, and also relates to a process for preparing such copolymers.

Copolymers comprising siloxane units and 10 oxyalkylene units are now well known and have been commercially employed in applications such as surfactants for polyurethane foams and as textile fibre lubricants. In U.K. Patent 1 290 687 there are disclosed siloxane-

- 15 polyoxyalkylene block copolymers in which there are present methoxy groups attached to silicon atoms. It is stated in the said patent that a preferred application of the block copolymers is in the treatment of hydrophobic
- 20 fibres to improve their soil resistance. European Patent Application 32 310 also discloses copolymers containing siloxane units, oxyalkylene units and silicon-bonded hydrolysable groups, and the use of such copolymers for
- 25 treating textiles. In the above described prior art copolymers the methoxy groups or hydrolysable groups are attached to a silicon atom in the siloxane chain either directly or by way of an aliphatic hydrocarbon linkage.

30 According to the present invention there are provided organosiloxane-oxyalkylene copolymers wherein at least one silicon atom of an organosiloxane unit has attached thereto a group represented by the general formula 35

40 wherein X represents a divalent hydrocarbon group having from 2 to 8 carbon atoms, R represents an alkylene group having from 2 to 4 carbon atoms, n is an integer of at least 2, Z represents an organic group composed of

45 carbon, hydrogen and oxygen and having therein at least one epoxy group, R' represents a lower alkyl, vinyl or phenyl group, R' represents an alkyl or an alkoxyalkyl group having less than 7 carbon atoms and a has a

naving less than 7 carbon atoms and a has a 50 value of 0 or 1, the remaining silicon-bonded substituents in the organosiloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula

-X(OR)\_OG

wherein X and R are as hereinbefore defined and G represents a hydrogen atom, a monova60 lent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms, at least 40 percent of the total substituents bonded to siloxane silicon atoms in the copolymer being methyl.
65 In the general formula above -(OR),- repre-

sents an oxyalkylene block having at least 2, preferably from 2 to 50 oxyalkylene units OR. The oxyalkylene units are preferably oxyethylene or oxypropylene or combinations of the two, for example—(OC<sub>2</sub>H<sub>4</sub>)<sub>8</sub>(OC<sub>3</sub>H<sub>8</sub>)<sub>6</sub>—. The group X which links the oxyalkylene block to the siloxane silicon atom may have from 2 to 8 carbons, but, in view of the more ready availability of the polyoxyalkylene precursor, is preferably the propylene group —(CH<sub>2</sub>)<sub>3</sub>.

The substituent Z is an epoxidised monovalent organic group composed of carbon, hydrogen and oxygen. Examples of such groups include the group

80

and those represented by the general formula

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wherein Q represents a divalent hydrocarbon 95 group e.g. ethylene, butylene, phenylene, cyclohexylene and

or an ether oxygen-containing group such as -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub> and -CH<sub>2</sub>CH<sub>2</sub>OCH(CH<sub>3</sub>)CH<sub>2</sub>-. Preferably Z represents the group

As the R" groups there may be present any alkyl or alkoxyalkyl group having less than 7 carbon atoms e.g. methyl, ethyl, propyl, methoxyethyl and ethoxyethyl, the preferred copolymers being those wherein R" represents methyl, ethyl or methoxyethyl. The R' groups, when present, may be C<sub>1-4</sub> alkyl, vinyl or 120 phenyl.

At least one of the above oxyalkylene-containing groups should be present in the copolymer. The number present in any particular case will depend upon such factors as the size of the copolymer molecule desired and the balance sought between the properties bestowed by the siloxane and oxyalkylene portions. The remaining substituents on the siloxane silicon atoms may be selected from hydro-

e.g. ethyl, propyl, 2,4,4-trimethylpentyl, vinyl, allyl and phenyl and silicon-free oxyalkylene groups of the formula –X(OR),OG, wherein G is for example ethyl, butyl or acetyl; with the proviso that at least 40 percent of the total siloxane silicon-bonded substituents are methyl groups. The preferred copolymers of this invention are those wherein the oxyalkylene groups (OR), are oxyethylene and comprise at 10 least 35% of the total weight of the copolymer.

The copolymers of this invention may take any of the molecular configurations available to such copolymers provided such configuration is consistent with the presence of terminal silyl groups on the oxyalkylene-containing group or groups. For example, they may be of the ABA configuration wherein A represents the

group and B represents a linear siloxane portion e.g. -(M<sub>2</sub>SiO)<sub>b</sub> wherein each M individually represents an organic substituent such as -CH<sub>3</sub> and b is an integer of at least 2. Alternatively the copolymer may be of the socalled "rake" configuration wherein the oxyal-sylene-containing groups are pendant from a siloxane chain as in

in which y is zero or an integer and z is an integer. According to yet another configura45 tion the oxyalkylene-containing (A) groups may be present both in the pendant positions and attached to the terminal silicon atoms of the siloxane chain. It will thus be apparent that in addition to the siloxane units having oxyalkylene groups attached thereto the copolymers of this invention may also comprise monofunctional M<sub>2</sub>SiO<sub>2</sub> units, difunctional M<sub>2</sub>SiO and trifunctional MSiO<sub>3/2</sub> units. If desired, small proportions of tetrafunctional SiO<sub>2</sub> units may also be present.

The copolymers of this invention can be obtained by reacting together (A) an organosiloxane-oxyalkylene copolymer wherein at least one silicon atom of an organosiloxane unit has 60 attached thereto a group of the general formula

65 the remaining silicon-bonded substituents in

the organo-siloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula –X(OR),OG, at least 40 percent of the total substituents-bonded-to siloxane siticon atoms in the copolymer being methyl groups, and (B) an organosilane

ZSiR'.(OR") ...

75

wherein X, R, Z, R', R" and a are as hereinbefore defined and G represents a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 80 6 carbon atoms.

Organosiloxane-oxyalkylene copolymers (A) employed in the said preparative process are a known class of materials. Such copolymers and methods for their preparation are described in, for example, British Patents 802 467 and 1 143 206. The silanes (B) are also known substances and have been disclosed in, for example, British Patent 834 326.

Some reaction between (A) and (B) to form the organosiloxane-oxyalkylene copolymers of this invention is believed to occur at normal ambient temperatures. It is preferred, however, to expedite the reaction by the use of 95 higher temperatures, for example, from about 60°C to 180°C. If desired the reaction may be carried forward in the presence of a transesterification catalyst, for example zinc tetrafluoroborate, an organic tin compound e.g. stan-100 nous octoate or a titanium compound e.g. tetrabutyl titanate. Where subsequent reaction of the copolymer via the epoxy groups is envisaged the preferred catalysts are those which also function to open the epoxy ring 105 e.g. zinc tetrafluoroborate.

The relative molar proportions of the reactants employed may be varied to achieve substantially complete reaction of the available COH groups, or to induce only partial reaction whereby the resulting copolymer product contains both silylated and non-silylated oxyalkylene groups.

The molecular weight of the copolymers of this invention may vary widely and the co-115 polymers may range from mobile liquids to gummy or waxy solids. When a sufficient proportion of oxyethylene units is present the copolymers are water-soluble. The copolymers may therefore be formed into curable films on 120 continuous, porous or fibrous substrates from aqueous or non aqueous solutions. Curing of the copolymers into films will take place in the absence of a curing catalyst. It is, however, generally preferred to accelerate the cure by 125 the addition of a siloxane condensation catalyst. A wide variety of such catalysts are known and include, for example acids, bases and metal organic compounds such as the metal carboxylates e.g. dibutyltin dilaurate, 130 stannous octoate and zinc octoate and titanium alkoxides and chelates. Certain substances e.g. zinc tetrafluoroborate and stannous octoate can function both as a transesterification catalyst during the preparation of the siloxane-oxyalkylene copolymer and subsequently as a curing catalyst therefor.

It is also preferred to effect drying and curing of the films at elevated temperatures. The actual temperature employed will depend 10 to some extent on the nature and heat resistance of the substrate, temperatures in the range from about 80°C to about 180°C being generally appropriate.

If desired the copolymers of the invention 15 may be mixed with fillers, pigments and other additives to produce compositions curable to rubbery solids having paintable surfaces.

The following examples in which Me represents methyl illustrate the invention.

Example 1

20

To a 20 litre split-necked flask equipped with a stirrer, condenser and thermometer was charged 12,500g of a siloxane-oxyalky-lene copolymer of average composition [HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>12</sub>(CH<sub>2</sub>)SiMe<sub>2</sub>O<sub>0.8</sub>]<sub>2</sub> (SiMe<sub>2</sub>O)<sub>14</sub>. The flask was heated to 90°C and a 40% by weight aqueous solution (26ml) of zinc tetrafluoroborate added and dissolved with stiraling. This was followed by the addition over 25 minutes of the silane.

(2458.7g), the reaction mixture then being maintained at 90°C for a further 2 hours. On 40 cooling there was obtained 14,870g (99.5%) of a clear, amber, water-soluble liquid.

When an aqueous solution (15% by weight) of the liquid was coated on to aluminium and dried at 150°C for 3 minutes a crosslinked, 45 water-insoluble, hydrophilic film was obtained.

Example 2

192G of the siloxane-oxyalkylene copolymer employed in Example 1 and 1gm of concentrated hydrochloric acid were heated with stirring to 90°C. 37.8g of the silane

were added and the mixture maintained at 90°C for 2 hours. On cooling there was 60 obtained 223g (97%) of a clear, amber, water-soluble liquid. When an aqueous solution (15% by weight) of the liquid was coated onto aluminium and dried for 3 minutes at 150°C a crosslinked 25 water insoluble film 65 was obtained.

Example 3

Employing the procedure of Example 1 a siloxane-oxyalkylene copolymer (240g) of av-

Me<sub>3</sub>Si(OSiMe<sub>2</sub>)<sub>e</sub>(OSiMe)<sub>3</sub>OSiMe<sub>3</sub>

(CH<sup>2</sup>)<sup>2</sup>(OC H<sup>2</sup>CH<sup>2</sup>),,OH

75 and the silane

(70.8g) were reacted at 90-100°C in the presence of a 40% by weight aqueous solution (3ml) of zinc tetrafluoroborate.

The reaction product (304g) was a clear, amber-coloured liquid which formed clear aqueous solutions. On drying these solutions (10% by weight) at 150°C for 3 minutes clear crosslinked hydrophilic films were obtained.

Example 4

150.9G of a siloxane-oxyalkylene copolymer having the average composition
[HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>7.5</sub>(CH<sub>2</sub>)<sub>3</sub>SiMe<sub>2</sub>O<sub>0.5</sub>]<sub>2</sub> (SiMe<sub>2</sub>O)<sub>4.5</sub>
was heated to 80°C with stirring. A 40% by
weight aqueous solution (2ml) of Zn(BF<sub>4</sub>)<sub>2</sub> was
then added, followed by 47.2g of the silane

100

105 The mixture was maintained at 80°C for 2 hours and then allowed to cool. A slightly hazy water-soluble liquid was obtained. When a 10% by weight aqueous solution of this liquid was dried at 150°C a crosslinked, 110 water-insoluble film resulted.

#### CLAIMS

 An organosiloxane-oxyalkylene copolymer wherein at least one silicon atom of an organosiloxane unit has attached thereto a group represented by the general formula

Z ! ! 20 –X(OR),,Osr;,(OR′′)<sub>2-</sub>,

wherein X represents a divalent hydrocarbon group having from 2 to 8 carbon atoms, R represents an alkylene group having from 2 to 4 carbon atoms, n is an integer of at least 2, Z represents an organic group composed of carbon, hydrogen and oxygen and having therein at least one epoxy group, R' represents a lower alkyl, vinyl or phenyl group, R"

represents an alkyl or an alkoxyalkyl group having less than 7 carbon atoms and a has a value of 0 to 1, the remaining silicon-bonded substituents in the organosiloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula

#### -X(OR),OG

10

wherein X and R are as hereinabove defined and G represents a hydrogen atom, a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms, at least 40 percent of the total substituents bonded to siloxane silicon atoms in the copolymer being methyl groups.

2. A copolymer as claimed in Claim 1 wherein the OR units are oxyethylene units or

20 oxypropylene units or both.

3. A copolymer as claimed in Claim 1 or Claim 2 wherein n has a value from 2 to 50.

 A copolymer as claimed in any one of the preceding claims wherein X represents the 25 group -(CH<sub>2</sub>)<sub>2</sub>-.

5. A copolymer as claimed in any one of the preceding claims wherein R" represents the methyl, ethyl or methoxyethyl group.

- A process for the preparation of an organosiloxane-oxyalkylene copolymer as defined in Claim 1 which comprises reacting together (A) an organosiloxane-oxyalkylene copolymer wherein at least one silicon atom of an organosiloxane unit has attached thereto a group represented by the general formula
  - -X(OR),OH

the remaining silicon-bonded substituents in 40 the organosiloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula

#### 45 -X(OR),OG

at least 40 percent of the total substituents bonded to siloxane silicon atoms in the copolymer being methyl groups, and (B) an 50 organosilane

#### ZSiR' (OR")3-0

- wherein X, R, Z, R', R" and a are as defined 55 in Claim 1 and G represents a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms.
- 7. A process as claimed in Claim 6 wherein there is present a transesterification catalyst.
  - 8. A process as claimed in Claim 7 wherein the catalyst is a substance which also effects ring opening of the epoxy group.
  - 9. A process for coating a substrate which

comprises applying thereto an organosiloxaneoxyalkylene copolymer as claimed in any one of Claims 1 to 5 inclusive.

 An organosiloxane-oxyalkylene copolymer as claimed in Claim 1 substantially as described with reference to the Examples herein.

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- (54) Organosilozane-oxyalkylene copolymers
- (57) Organosiloxane-exyalkylene copolymers in which at least one silicon atom of an erganosiloxane unit has attached thereto a group

-X(OR),OSIR',(OR")2.

In which X is a divalent hydrocarbon group, R is an alkylene group, n is an integer of at least 2, Z is an organic substituent containing an epoxy group, R' is lower alkyl, vinyl or phenyl, R" is alkyl or alkoxyalkyl and a is 0 or 1, at least 40 percent of the total substituents in the copolymer boing methyl. The copolymers are film forming and may be applied to continuous or porous substrates from equeous or non-equeous solutions.

#### SPECIFICATION

#### Organosilozane-oxyalkylene copolymers

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Copolymers comprising allocane units and oxyalkylane units are now well known and have been commercially employed in applications such as surfaceants for polyurethane foams and as textile fibre jubricants. In U.K. Patent 1 290 687 there are disclosed siloxane-

15 polyoxyalkylene block copolymers in which there are present methoxy groups attached to silicon atoma. It is stated in the said patent that a preferred application of the block copolymers is in the treatment of hydrophobic

20 fibres to improve their soil resistance. European Patent Application 32 310 elso discloses copolymers containing siloxane units, oxyalkylene units and silicon-bonded hydrolysable groups, and the use of such copolymers for

25 treating taxtiles. In the above described prior art copolymers the methoxy groups or hydrolysable groups are attached to a silicon atom in the siloxane chain either directly or by way of an sliphatic hydrocarbon linkage.

According to the present invention there are provided organosiloxane-oxyalkylene co-polymers wherein at least one silicon atom of an organosiloxane unit has attached thereto a group represented by the general formula

2 -X(OR),OSIR',(OR")

40 wherein X represents a divalent hydrocarbon group having from 2 to 8 carbon atoms, R represents an alkylene group having from 2 to 4 carbon atoms, n is an integer of at least 2, 2 represents an omegic commitment of the carbon atoms.

Z represents an organic group composed of 45 carbon, hydrogen and oxygen and having therein at least one spoxy group, R' represents a lower sikyl, vinyl or phenyl group, R' represents an sikyl or an alkoxyalkyl group having leas than 7 carbon atoms and a has a

50 value of 0 or 1, the remaining silicon-bonded substituents in the organosiloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula

-X(OR)\_OG

wherein X and R are as hereinbefore defined and G represents a hydrogen atom, a monove60 lent hydrocarbon group heving from 1 to 10 carbon stams or an ecyl group having from 2 to 6 carbon stams, at least 40 percent of the total substituents bended to siloxene silicon stams in the copolymer being methyl.

in the general formula above -(OR), - repre-

sents an oxyalkylene block having at least 2, preferably from 2 to 50 oxyalkylene units OR. The oxyalkylene units are preferably oxyethylene or oxypropylene or combinations of the 100, for example-(OC<sub>2</sub>H<sub>2</sub>)<sub>6</sub>(OC<sub>2</sub>H<sub>2</sub>)<sub>6</sub>. The group X which links the oxyalkylene block to the siloxene silicon stom may have from 2 to 8 carbons, but, in view of the more ready availability of the polyoxyalkylene precursor, is preferably the propylene group -(CH<sub>2</sub>)<sub>1</sub>.

The substituent Z is an epoxidised monovalem organic group composed of carbon, hydrogen and oxygen. Examples of such groups

include the group

and those represented by the general formula

85

wherein Q represents a divatent hydrocarbon group e.g. ethylens, butylens, phonylens, cyclohexylens and

or an other oxygen-containing group such as -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> and -CH<sub>2</sub>CH<sub>3</sub>OCH(CH<sub>3</sub>)CH<sub>2</sub>-. Preferably Z represents the group

As the R" groups there may be present any slicyl or alkoxyalkyl group having less than 7 carbon atoms e.g. methyl, ethyl, propyl, methoxyethyl and ethoxyethyl, the preferred copolymers being those wherein R" represents methyl, athyl or methoxyethyl. The R' groups, when present, may be C<sub>1-4</sub> alkyl, vinyl or 120 phenyl.

At least one of the above exystkylene-containing groups should be present in the copolymer. The number present in any particular case will depend upon such factors as the size of the copolymer molecule desired and the balance sought between the properties bestowed by the siloxene and exystkylene pertions. The remaining substituents on the siloxene silicon atoms may be selected from hydro-

130 gen atoms, monovalent hydrocarbon groups

e.g. ethyl, propyl, 2,4,4-trimethylpentyl, vinyl, allyl and phenyl and silicon-free oxygikylene groups of the formula —X(OR),OG, wherein G is for example ethyl, butyl or acetyl; with the proviso that at least 40 percent of the total siloxane silicon-bonded substituents are methyl groups. The preferred copolymers of this invention are those wherein the oxygikylene groups (OR), are oxyethylene and comprise at

10 least 35% of the total weight of the copolymer.

any of the molecular configurations available to such copolymers provided such configura15 tion is consistent with the presence of terminal silyl groups on the axyalkylane-containing group or groups. For example, they may be of the ABA configuration wherein A represents the

The copolymers of this invention may take

group and B represents a linear siloxane pertion e.g. —(M<sub>2</sub>SiO), wherein each M individually represents an organic substituent such as —CH<sub>2</sub> and b is an integer of at least 2. Alternativaly the copolymer may be of the socalled "rake" configuration wherein the oxyal-SO kylene-containing groups are pendant from a siloxane chain as in

In which y is zero or an integer and z is an integer. According to yet another configuretion the exyelkylene-containing (A) groups may be present both in the pendant positions and attached to the terminal silicon stoms of the siloxane chain. It will thus be apparent that in addition to the siloxane units having exyelkylene groups attached thereto the co-polymers of this invention may also comprise monofunctional M<sub>3</sub>SiO, units, difunctional M<sub>2</sub>SiO and trifunctional MSiO<sub>3/2</sub> units. If desired, small proportions of tetrafunctional SiO<sub>2</sub> units may also be present.

The copolymers of this invention can be obtained by reacting together (A) an organosioxane-oxyalkylene copolymer wherein at least one silicon atom of an organosiloxane unit has so attached thereto a group of the general formula.

85 the remaining silicon-bonded substituents in

the organo-siloxane units being selected from hydrogen stome, monovelent hydrocarbon groups and groups represented by the general formula —X(OR), OG, et least 40 percent of the total substituents bonded to siloxane silicon atoms in the copolymer being methyl groups, and (B) an organosilane

ZSiR',(OR"),

75

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Organoslozzne-czysikylene copolymers (A) employed in the said preparative process are a known class of materials. Such copolymers and methods for their preparation are described to the communication are described.

85 acribed in, for example, British Patenta 802487 and 1 143208. The silenes (B) are also known substances and have been disclosed in, for example, British Patent 834328.

Same reaction between (A) and (B) to form the organosiloxane-oxyalkylene copolymers of this invention is believed to occur at normal ambient temperatures. It is preferred, however, to expedite the reaction by the use of 95 higher temperatures, for example, from about 60°C to 180°C. If desired the reaction may be carried forward in the presence of a transesterification catalyst, for example zinc tetrafluoroborate, an organic tin compound e.g. stan-100 nous actoste or a titenium compound e.g. tetrabutyl titanate. Where subsequent reaction of the copolymer via the epoxy groups is anvisaged the preferred catalysts are those which also function to open the apoxy ring 105 e.g. zinc tetrafluoroborate.

The relative molar proportions of the resotants employed may be varied to achieve substantially complete reaction of the available COH groups, or to induce only partial reaction whereby the resulting copolymer product contains both silylated and non-silylated oxyalkylene groups.

The molecular weight of the copolymers of this invention may vary widely and the copolymers may range from mobile liquids to gummy or waxy solids. When a sufficient proportion of oxyethylene units is present the copolymers are water-soluble. The copolymers may therefore be formed into curable films on continuous, porous or fibrous substrates from aqueous or non aqueous solutions. Curing of the copolymers into films will take place in the absence of a curing catalyst. It is, however,

generally preferred to accelerate the cure by the addition of a silozene condensation catalyst. A wide variety of such catalysts are known and include, for example acids, bases and metal organic compounds such as the metal carboxylates e.g. dibutyitin dilaurate, 130 stannous octoste and sinc octoste and titan-

lum alkoxides and chelates. Certain substances e.g. zine tetrafluoroborate and stannous octoste can function both as a transest-erification catalyst during the preparation of the alloxens-oxyalkylene copolymer and subsequently as a curing catalyst therefor.

It is also preferred to effect drying and curing of the films at elevated temperatures. The actual temperature employed will depend to some extent on the nature and heat reeletance of the substrate, temperatures in the range from about 80°C to about 180°C being generally appropriate.

If desired the copolymers of the invention 15 may be mixed with fillers, pigments and other additives to produce compositions curable to subbery solids having paintable surfaces.

The following examples in which Me represents methyl illustrate the invention.

Example 1

20

To a 20 litre split-necked flask equipped with a stirrer, condenser and thermometer was charged 12,500g of a slioxane-oxyalky-lene copolymer of average composition [HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>12</sub>(CH<sub>2</sub>)SiMe<sub>2</sub>O<sub>0.0</sub>]<sub>2</sub> (SiMe<sub>2</sub>O)<sub>14</sub>. The flask was heated to 90°C and a 40% by weight aqueous solution (28mi) of zinc tetrafluoroborste added and dissolved with stirring. This was followed by the addition over 25 minutes of the silane.

(2458.7g), the reaction mixture then being maintained at 90°C for a further 2 hours. On 40 cooling there was obtained 14,870g (99.5%) of a clear, amber, water-soluble liquid.

When an aqueous solution (15% by weight) of the liquid was coated on to aluminium and dried at 150°C for 3 minutes a crosslinked, 45 water-insoluble, hydrophilic film was obtained.

Example 2

192G of the siloxans-oxyalkylene copolymer employed in Example 1 and 1gm of concentrated hydrochloric acid were heated with stirring to 80°C. 37.8g of the silene

were added and the mixture maintained at 90°C for 2 hours. On cooling there was obtained 223g (97%) of a clear, amber, water-soluble liquid. When an equeous solution (15% by weight) of the liquid was coated onto aluminium and dried for 3 minutes at 150°C a crosslinked 25 water insoluble film 65 was obtained.

Example 3

Employing the procedure of Example 1 a slioxane-cayalkylene copolymer (240g) of average composition

MozSi(OSiMoz)o(OSiMo)zOSIMoz

(CH3)\*(OÇ H\*CH3)"OH

and the allene

75

80 (MeO) 381 (CH2) 30CH2 CH - CH2

(70.8g) were reacted at 80–100°C in the presence of a 40% by weight aqueous solution (3ml) of zinc tetrafluoroborate.

The reaction product (304g) was a clear, amber-coloured liquid which formed clear aqueous solutions. On drying these solutions (10% by weight) at 150°C for 3 minutes clear crosslinked hydrophilic films were obtained.

Exemple 4

150.9G of a siloxane-oxyalkylens copolymer having the everage composition

95 [HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>7.5</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>2</sub>O<sub>0.1</sub>]<sub>2</sub> (SiMe<sub>2</sub>O)<sub>4.5</sub>

was heated to 80°C with stirring. A 40% by
weight aqueous solution (2mi) of Zn(BF<sub>4</sub>)<sub>2</sub> was
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CLAIMS

 An organosiloxane-oxyalkylene copolymer wherein at least one silicon atom of 115 an organosiloxane unit has attached thereto a group represented by the general formula

Z 120 -x(OR),Osx,(OR')2--

wherein X represents a divalent hydrocarbon group having from 2 to 8 carbon stoms, R represents an alkylene group having from 2 to 4 carbon atoms, n is an integer of at least 2, Z represents an organic group composed of carbon, hydrogen and exygen and having therein at least one epoxy group, R' represents a lower alkyl, vinyl or phenyl group, R"

represents an alkyl or an alkoxyalkyl group having less than 7 carbon atoms and a has a value of 0 to 1, the remaining silicon-bonded substituents in the organosiloxene units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula

#### ---X(OR),OG

wherein X and R are as hereinabove defined and G represents a hydrogen atom, a monovelent hydrocarbon group having from 1 to 10 cerbon atoms or an acyl group having from 2

15 to 6 carbon atoms, at least 40 percent of the total substituents bonded to alloxane allicon atoms in the copolymer being methyl groups.

2. A copolymer as claimed in Claim 1 wherein the OR units are oxyethylene units or 20 exypropylene units or both.

A copolymer as claimed in Claim 1 or Claim 2 wherein n has a value from 2 to 50.

4. A copolymer as claimed in any one of the preceding claims wherein X represents the 25 group -(CH2)3-.

5. A copolymer as claimed in any one of the preceding claims wherein R" represents the methyl, ethyl or methoxyethyl group.

6. A process for the preparation of an 30 organosiloxene-oxysikylene copolymer as defined in Claim 1 which comprises reacting together (A) an organosiloxane-oxyalkylene copolymer wherain at least one silicon atom of an organosiloxane unit has attached thereto a 35 group represented by the general formula

#### -X(OR),OH

the remaining silicon-bonded substituents in 40 the organosiloxane units being selected from hydrogen atoms, monovelent hydrocerbon groups and groups represented by the general formula

#### 45 -X(OR), OG

at least 40 percent of the total substituents bonded to alloxane allicon atoms in the copolymer being methyl groups, and (B) an 50 organosilane

#### ZSir',(Or"),\_

wherein X. R, Z, R', R" and a are as defined 55 in Claim 1 and G represents a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms.

7. A process as claimed in Claim 6 60 wherein there is present a transesterification catalyst.

8. A process as claimed in Claim 7 wherein the catalyst is a substance which also effects ring opening of the spoxy group.

9. A process for coating a substrate which

comprises applying thereto an organosiloxaneoxyalkylene copolymer as claimed in any one of Claims 1 to 5 inclusive.

10. An organosiloxane-oxyalkylene co-70 polymer as disimed in Claim 1 substantially as described with reference to the Exemples herein.

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#### (54) Organosiloxane-oxyalkylene copolymers

(57) Organoziloxane-oxyalkylene copolymers in which at least one ellicon atom of an organosiloxane unit has attached thereto a group

Z | -X(OR),OSIR',(OR'');

in which X is a divalent hydrocarbon group, R is an alkylene group, n is an integer of at last 2, Z is an organic substituent containing an epoxy group, R' is lower alkyl, vinyl or phenyl, R" is alkyl or alkoxyalkyl and a is 0 or 1, at least 40 percent of the total substituents in the copelymer being methyl. The copolymers are film forming and may be applied to continuous or porous substrates from equeous or non-equeous solutions.

#### SPECIFICATION

#### Organosilozane-ozyalkylene copolymers

5 This invention relates to copolymers comprising organositoxane units and oxyalkylene units, and also relates to a process for preparing such copolymers.

Copolymers comprising alloxane units and 10 oxyalkylene units are now well known and have been commercially employed in applications such as surfactants for polyurethane feams and as textile fibre lubricants. In U.K. - Patent 1 290 687 there are disclosed slioxane-

15 polyoxyalkylene block copolymers in which there are present methoxy groups attached to silicon atoms. It is stated in the said patent that a preferred application of the block copolymers is in the treatment of hydrophobic

20 fibres to improve their soil resistance. European Patent Application 32 310 also discloses copolymers containing silozane units, oxyalkylene units and silicon-bonded hydrolysable groups, and the use of such copolymers for

25 treating taxtiles. In the above described prior art copolymers the methoxy groups or hydrolysable groups are attached to a silicon atom in the siloxane chain either directly or by way of an sliphatic hydrocarbon linkage.

According to the present invention there are provided organosiloxane-oxyalkylene copolymers wherein at least one silicon atom of an organosiloxane unit has attached thereto a group represented by the general formula

40 wherein X represents a divalent hydrocarbon group having from 2 to 8 carbon atoms, R represents an alkylene group having from 2 to 4 carbon atoms, n is an integer of at least 2, Z represents an organic group composed of

45 carbon, hydrogen and oxygen and having therein at least one spoxy group, R' represents a lower alkyl, vinyl or phenyl group, R" represents an alkyl or an alkoxyalkyl group having less than 7 carbon atoms and a has a

50 value of 0 or 1, the remaining silicon-bonded substituents in the organosiloxane units being selected from hydrogen stoms, monovalent hydrocarbon groups and groups represented by the general formula

#### -X(OR)\_OG

wherein X and R are as hereinbefore defined and G represents a hydrogen atom, a monove60 lent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms, at least 40 percent of the total substituents bended to alloxane silicon atoms in the copolymer being methyl.

65 In the general formula above -(OR), - repre-

sents an exyalkylene block having at least 2, preferably from 2 to 50 exyalkylene units OR. The exyalkylene units are preferably exyethylene or exypropylene or combinations of the 10 two, for example-(OC<sub>2</sub>H<sub>2</sub>)<sub>6</sub>(OC<sub>2</sub>H<sub>2</sub>)<sub>6</sub>. The group X which links the exyalkylene block to the allexane allicon atom may have from 2 to 8 carbona, but, in view of the more ready sveilability of the polyexyalkylene procursor, is preferably the propylene group -(CH<sub>2</sub>)<sub>2</sub>. The substituent Z is an epoxidised moneye-

The substituent Z is an epoxidized monovalent organic group composed of carbon, hydrogen and oxygen. Examples of such groups include the group

and those represented by the general formula

wherein Q represents a divalent hydrocarbon 95 group e.g. ethylene, butylene, phenylene, cyclohexylene and

or an ether oxygen-containing group such as -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub> and -CH<sub>2</sub>CH<sub>3</sub>OCH(CH<sub>3</sub>)CH<sub>3</sub>-. Preferably Z represents the group

As the R" groups there may be present any slkyl or alkoxyalkyl group having less than 7 carbon atoms e.g. methyl, ethyl, propyl, methoxyethyl and athoxyethyl, the preferred co-polymers being those wherein R" represents methyl, athyl or methoxyethyl. The R' groups, when present, may be C<sub>1-4</sub> alkyl, vinyl or 120 phenyl.

At least one of the above oxyalkylene-containing groups should be present in the co-polymer. The number present in any particular case will depend upon such factors as the size of the capalymer molecule desired and the balance sought between the properties bestowed by the siloxane and oxyalkylene portions. The remaining substituents on the slioxane silicon atoms may be selected from hydro-130 gen stoms, monovalent hydrocarbon groups

e.g. ethyl, propyl, 2,4,4-trimethylpentyl, vinyl, allyl and phenyl and silicon-free oxysikylene groups of the formula —X(OR),OG, wherein G is for example ethyl, butyl or acetyl; with the proviso that at least 40 percent of the total alloxane silicon-bonded substituents are methyl groups. The preferred copolymers of this invention are those wherein the oxysikylene groups (OR), are oxysthylene and comprise at 10 least 35% of the total weight of the copolymer.

The copolymers of this invention may take any of the molecular configurations available to such copolymers provided such configuration is consistent with the presence of terminal silyl groups on the cayalkylene-containing group or groups. For example, they may be of the ABA configuration wherein A represents

group and B represents a linear siloxane por-28 tion e.g. —(M<sub>2</sub>SiO), wherein each M individually represents an organic substituent such as —CH<sub>3</sub> and b is an integer of at least 2. Alternativaly the copolymer may be of the socalled "rake" configuration wherein the oxyal-30 kylene-containing groups are pendant from a alloxane chain as in

In which y is zero or an integer and z is an integer. According to yet another configure-45 tion the exysikylene-containing (A) groups may be present both in the pendant positions and attached to the terminal silicon atoms of the siloxane chain. It will thus be apparent that in addition to the siloxane units having exysikylene groups attached thereto the copolymers of this invention may also comprise monofunctional M<sub>2</sub>SiO, units, difunctional M<sub>2</sub>SiO and trifunctional MSiO<sub>2/2</sub> units. If desired, small proportions of tetrafunctional SiO<sub>2</sub> units may also be present.

The copolymers of this invention can be obtained by reacting together (A) an organosi-ioxano-oxyalkylene copolymer wherein at least-one silicon atom of an organosiloxane unit has strached thereon a group of the general formula.

85 the remaining silicon-bonded substituents in

the organo-siloxane units being selected from hydrogen stome, monovelent hydrocarbon groups and groups represented by the general formula -X(OR),OG, at least 40 parcent of the total substituents bonded to alloxane silicon atoms in the copolymer being methyl groups, and (B) an organosilane

ZSiR' (OR"),

75

wherein X, R, Z, R', R" and a are as hereinbefore defined and G represents a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 80 6 carbon atoms.

Organosiloxane-oxysikylene copolymers (A) employed in the said preparative process are a known class of materials. Such copolymers and methods for their preparation are described in, for example, British Patents 802 487 and 1 143 208. The silanes (B) are also known substances and have been disclosed in, for example, British Patent 834 328.

Some reaction between (A) and (B) to form the organosiloxane-oxyalkylene copolymers of this invention is believed to occur at normal emblent temperatures. It is preferred, however, to expedite the reaction by the use of 95 higher temperatures, for example, from about 60°C to 180°C. If desired the reaction may be carried forward in the presence of a transasterification catalyst, for example zinc tetrafluoroborate, an organio tin compound e.g. stan-100 hous octoate or a titanium compound e.g. tetrabutyl titenate. Where subsequent reaction of the copolymer via the spoxy groups is envisaged the preferred catalysts are those which also function to open the epoxy ring 105 e.g. zine tetrafluoroborate.

The relative molar proportions of the resotants employed may be varied to achieve substantially complete reaction of the available COH groups, or to induce only partial 110 reaction whereby the resulting copolymer product contains both silylated and non-silylated oxyalkylene groups.

The molecular weight of the copolymers of this invention may vary widely and the co115 polymers may range from mobile liquids to gummy or waxy solids. When a sufficient proportion of expethylene units is present the copolymers are water-soluble. The copolymers may therefore be formed into curable films on 120 continuous, porous or fibrous substrates from aqueous or non aqueous solutions. Curing of the copolymers into films will take place in the absence of a curing catalyst. It is, however, generally preferred to accelerate the cure by the addition of a silexane condensation catalyst. A wide variety of such catalysts are known and include, for example acids, bases

and metal organic compounds such as the metal carboxylates e.g. dibutyitin dilaurate, 130 stannous octoate and zine octoate and than-

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lum alkoxides and chalates. Certain substances e.g. zine tetrafluoroborate and stannous octoate can function both as a transcaterification catalyst during the preparation of 5 the elloxene-oxyalkylene copolymer and subsequently as a curing catalyst therefor.

It is also preferred to effect drying and curing of the films at elevated temperatures. The actual temperature employed will depend 10 to some extent on the nature and heat realstance of the substrate, temperatures in the range from about 80°C to about 180°C being generally appropriate.

If desired the copolymers of the invention 15 may be mixed with fillers, pigments and other additives to produce compositions curable to rubbery solids having paintable surfaces.

The following examples in which Me represents methyl illustrate the invention.

Example 1

20

To a 20 litre split-necked flask equipped with a stirrer, condenser and thermometer was charged 12,500g of a siloxane-oxysiky-25 lene copolymer of average composition [HO(CH2CH2O),2(CH2)SiMe2O06], (SIMe2O),4 The flask was heated to 90°C and a 40% by weight aqueous solution (28ml) of zinc tetraffuoroborate added and dissolved with attr-30 ring. This was followed by the addition over 25 minutes of the sliane.

(2458.7g), the reaction mixture then being maintained at 90°C for a further 2 hours. On 40 cooling there was obtained 14,870g (99.5%) of a clear, amber, water-soluble liquid.

When an aqueous solution (15% by weight) of the liquid was costed on to aluminium and dried at 150°C for 3 minutes a crosslinked,

45 water-insoluble, hydrophilic film was obtained.

Example 2

192G of the siloxane-oxyelkylene copolymer employed in Example 1 and 1gm of concer-50 trated hydrochloric acid were heated with atinring to 90°C. 37.Bg of the allene

were added and the mixture maintained at 90°C for 2 hours. On cooling there was 80 obtained 223g (97%) of a clear, amber, water-soluble liquid. When an aqueous solution (15% by weight) of the liquid was coated onto aluminium and dried for 3 minutes at 150°C a crosslinked 25 water insoluble film 65 was obtained.

Example 3

Employing the procedure of Example 1 a alloxene-oxyalkylene copolymer (240g) of everage composition

Me,SI(OSiMe,),(OSiMe),OSIMe,

(CH1)\*(OC H\*CH3)12OH

and the allene

75

(70.8g) were reacted at 90-100°C in the presence of a 40% by weight aqueous solu-85 tion (3ml) of zine tetrafluoroborate.

The reaction product (304g) was a clear, amben-coloured liquid which formed clear aqueous solutions. On drying these solutions (10% by weight) at 150°C for 3 minutes clear 90 crosslinked hydrophilic films were obtained.

Exemple 4

150.9G of a silozane-oxyalkylene copolymer having the average composition 95 [HO(CH<sub>2</sub>CH<sub>3</sub>O)<sub>7,8</sub>(CH<sub>3</sub>)<sub>3</sub>8IMe<sub>2</sub>O<sub>0,2</sub>]<sub>2</sub> (SiMe<sub>3</sub>O)<sub>4,8</sub> was heated to 80°C with stirring. A 40% by weight aqueous solution (2ml) of Zn(BF4), was then added, followed by 47.2g of the silane

100

105 The mixture was maintained at 80°C for 2 hours and then allowed to cool. A slightly hazy water-soluble liquid was obtained. When a 10% by weight aqueous solution of this liquid was dried at 150°C a crosslinked, 110 water-insoluble film resulted.

CLAIMS

1. An organosiloxane-oxyaikylene copolymer wherein at least one silicon atom of an organosiloxane unit has attached thereto a group represented by the general formula

Z 120 -X(OR),Osx,(OR')2-

wherein X represents a divisiont hydrocarbon group having from 2 to 8 carbon atoms, R represents an alkylene group having from 2 to 125 4 carbon atoms, n is an integer of at least 2, Z represents an organic group composed of carbon, hydrogen and oxygen and having therein at least one epoxy group, R' represents a lower alkyl, vinyl or phonyl group, R"

represents an alkyl or an alkoxyalkyl group having less than 7 carbon atoms and a has a value of 0 to 1, the remaining silicon-bonded substituents in the organosiloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula

#### -X(OR),OG

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atoms in the copolymer being methyl groups.

2. A copolymer as claimed in Claim 1 wherein the OR units are oxyethylene units or

20 exypropylene units or both.

3. A copolymer as claimed in Claim 1 or Claim 2 wherein n has a value from 2 to 50.

 A copolymer as claimed in any one of the preceding claims wherein X represents the 25 group —(CH<sub>2</sub>)<sub>2</sub>—.

5. A copolymer as claimed in any one of the preceding claims wherein R" represents the methyl, ethyl or methoxyethyl group.

6. A process for the preparation of an organosiloxane-oxyalkylene copolymer as defined in Claim 1 which comprises reacting together (A) an organosiloxane-oxyalkylene copolymer wherein at least one silicon atom of an organosiloxane unit has attached thereto a 35 group represented by the general formula.

#### -X(OR),OH

the remaining silicon-bonded substituents in 40 the organosiloxane units being selected from hydrogen atoms, monovalent hydrocerbon groups and groups represented by the general formula

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#### ZSIR'\_(OR") --

wherein X. R, Z. R', R" and a are as defined 55 in Claim 1 and G represents a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms.

7. A process as claimed in Claim 6
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comprises applying thereto an organosiloxaneoxyalkylene copolymer as claimed in any one of Claims 1 to 5 inclusive.

10. An organosilozane-oxyalkylene co-70 polymer as claimed in Claim 1 substantially as described with reference to the Examples herein.

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